Flax Fiber-Reinforced Composites: The Influence of Fiber Surface Chemical Treatment on Mechanical Performance

B. Wang[1], S. Panigrahi[1], L. Tabil[1], W. Crerar[1]

[1]Department of Agricultural and Bioresource Engineering, University of Saskatchewan, Saskatoon, SK, S7N 5A9

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Abstract

Flax fibers can be used as environmentally-friendly alternatives to conventional reinforcing fibers (e.g., glass fiber) in composites. Flax fibers are less dense than glass fibers, are renewable and combustible (for easy disposal of composites), and are relatively low in price. This excellent price-performance ratio at low weight in combination with the environmentally friendly character is very important for the acceptance of natural fibers in large volume engineering markets. A major restriction to the successful use of natural fibers in durable composite applications is their high moisture absorption and poor dimensional stability. In order to improve their interfacial properties, fibers were subjected to different chemical modifications such as mercerization, silane treatment, benzoylation, and peroxide treatment. Selective removal of non-cellulosic compounds constitutes the main objective of the chemical treatments of flax fibers. Chemical treatments are able to induce fiber modifications that increase their resistance when utilized in composite products. Mechanical properties of untreated and treated fibers based composites were investigated.

Introduction

Saskatchewan's economy is largely dependent on agriculture. Diversification of the industry is crucial to encourage economic stability and growth. Value-added processing of various agricultural products is one example of such diversification. The goal of value-added processing is to find new uses for agricultural materials which are currently shipped away for processing, or disposed of post-harvest.

Flax is an oilseed crop grown throughout Saskatchewan. While the seed is processed for its high oil content, the biomass left behind tends to be a problem. Traditionally, flax straw has been burned by farmers, as it has strong fibers which breakdown very slowly under natural conditions. The goal of this work is to find a more environmentally responsible use for flax straw.

Traditional plastic materials are reinforced by glass fibers, which are both expensive and harmful to the environment. Biocomposite material contains polymers reinforced with flax fiber. There are a number of reasons for this; flax fiber will make the material partially biodegradable, glass

is relatively expensive to make, flax is currently disposed of by burning, flax has extremely high tensile strength, this will allow for agricultural diversification within Saskatchewan, etc. Over the past decade, cellulosic fillers of a fibrous natural have been of greater interest as they would give composites with improved mechanical properties compared to those containing non-fibrous fillers. Published data show that various commercial wood fibers have good potential as reinforcements in thermoplastics. Cazaurang et al. pointed out that these hard fibers posses mechanical properties that make them a suitable candidate to reinforce thermoplastic resins. Woodhams *et al.* reported that polypropylene composites containing 40-50% wood fiber cost effective alternative to many filled plastics metals in terms of bending stiffness or weight. Raj *et al.* have studied the mechanical properties of wood fiber filled medium density polyethylene (MDPE) composites. They observed a significant increase in modulus with increase in filler content. The mechanical properties of low density polyethylene reinforced with silane treated wood pulps and polyethylene grafted wood pulps were compared by Beshay *et al.*. They found the grafted CTMP fibers improved the mechanical properties of the composite by a factor of 2.6 for modulus, 2.3 for stress, and 2.1 for energy at yield.

The creation of fiber-reinforced composites is a multi-step process. The flax fiber is collected as straw, and chemical treatments are used to reduce it to its fibrous form. The fibers are chopped to appropriate length, and combined with synthetic polymer materials. A series of techniques including extrusion and rotational molding are used to develop the final product. Eventually Flaxtic will be marketed in the storage sector.

Flaxtic has material properties similar to that of conventional plastic products. In time, our vision is that an industry centered on the processing of flax fiber will develop. Work in this area has begun, and the research within our department continues. The environmental benefits of Flaxtic (as a use for biomass) are appealing to producers, consumers, and industry alike.

Materials and Methods

Material Preparation

Flax fibers were derived from linseed flax grown in Saskatchewan and decorticated on a standard scutching mill at Durafiber in Canora, SK, Canada. The fibers were first washed thoroughly with 2% detergent water and dried in an air oven at 70ºC for 24 h. The dried fibers were designated as untreated fibers. Flax fibers were then subjected to sequential extraction with 1:2 mixture of ethanol and benzene for 72 h at 50ºC, followed by washing with double distilled water and air drying to remove waxes and water soluble polymers prior to chemical treatments. Reagent grade chemicals were used for fiber surface modifications, namely, sodium hydroxide (NaOH), benzoyl chloride, ethanol, dicumyl peroxide, acetone, alcohol and the coupling agent, triethoxyvinylsilane (Aldrich Chemical Co. Ltd.).

In this series of experiments, high-density polyethylene, linear low-density polyethylene (HDPE 8761.27 and LLDPE 8460.29, Exxon Mobil, Toronto, ON) and LLDPE/HDPE 25087 (NOVA Chemicals Ltd., Calgary, AB) were used as major polymer matrix materials.

Fiber Surface Treatment

Generally, the first step is the mercerization process (pre-treatment process) for all of fiber surface treatments which causes changes in the crystal structure of cellulose. Fibers were soak in 5-18% NaOH (silane treatment: 5% NaOH, benzoylation: 18%, peroxide treatment: 10%) for about half an hour in order to activate the OH groups of the cellulose and lignin in the fiber. Fibers were then washed many times in distilled water and finally dried. Then the different chemicals can be used on the fibers surface in order to improve the interfacial properties.

Silane treatment: The pre-treated fibers were dipped in alcohol water mixture (60:40) containing triethoxyvinylsilane coupling agent. The pH of the solution was maintained between 3.5 and 4, using the METREPAK Phydrion buffers and pH indicator strips. Fibers were washed in double distilled water and dried in the oven.

Benzoylation: The treated fibers were suspended in 10% NaOH solution and agitated with benzoyl chloride. The mixture was kept for 15 min, filtered, washed thoroughly with water and dried between filter papers. The isolated fibers were then soaked in ethanol for 1 h to remove the untreated benzoyl chloride and finally were washed with water and dried.

Peroxide treatment: Pre-treated fibers were coated with dicumyl peroxide from acetone solution after alkali pre-treatments. Saturated solution of the peroxide in acetone was used. High temperature is favored for decomposition of the peroxide.

Composite Preparation

Pre-treated and untreated fibers were ground by the grinding mill (Falling Number, Huddinge, Sweden) and oven dried at 80°C for 24 h to reduce the moisture content to less than 2%. Mixtures of thermoplastic powder and 10% and 20% by weight of flax fibers were prepared by using a food blender (Waring Products Corporation, New York, NY). This was done to aid in homogeneous mixing of fibers and thermoplastics during extrusion process. Silane-coupling agents were added at a rate of 5% by weight as “resin additive”. The blend was fed to the twin-screw extruder (Werner & Pfleiderer, Ramsey, NJ) at the Centre for Agri-Industrial Technology (CAIT) in Edmonton, AB using a barrel to die temperature profile of 175°C. Blends prepared in this manner were extruded using a strand die. Extruded strands were then pelletized. The pellets were ground using a grinding mill (Retsch GmbH 5657 HAAN, West Germany) and the ground product was used in rotational molding.

Biocomposites Manufacturing by Rotational Molding

Test samples were prepared from ground extruded pellets using a rotational molding machine at Parkland Plastics in Saskatoon, SK. It is a carousel-type molding machine with four separate arms that can each rotate at two separate axes, while completely enclosed in an oven at 250°C for 30 min. Single large mold cavities can be placed on each arm or many smaller shapes.

Tensile Test

Tensile test, in a broad sense, is a measure of the ability of a material to withstand forces that tend to pull it apart. It determines to what extent the material stretches before breaking. Tensile

property data are more useful in preferential selection of a particular type of plastic from a large group of plastic materials.

Specimens were conditioned for 7 days at 23°C and 50% relative humidity prior to performing tensile tests. Composites having 10% and 20% fiber by weight loading were prepared and properties were evaluated by mechanical tests. The appropriate ASTM methods were followed, and at least five replicate specimens were tested and the results were presented as average of tested specimens. The test conducted at standard laboratory atmosphere of 23°C and 50% relative humidity.

The familiar dog-bone shape of the rotationally molded sample was utilized in the testing procedure. This type I specimen was the preferred specimen and should be used where sufficient material having a thickness of 7 mm or less is available. An Instron Universal testing machine (SATEC Systems, Inc., Grove City, PA) was used to perform the tensile strength test at a crosshead speed of 5 mm/min as described in ASTM procedure D638-99 (ASTM 1999), and each test was performed until tensile failure occurred. The maximum (peak) load value (force) (F_{max}) was recorded by the instrument, which can be recalled after the completion of the test. The tensile strength at yield (σ_{ty}) is calculated from the following:

$$\sigma_{ty} = \frac{F_{max}}{A} \qquad (1)$$

Where A is the cross sectional area. The picture of tensile testing machine and specimen is given in Figure 1.

Fig.1. Tensile test using Instron testing machine.

Durometer Hardness

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation, or scratching. The Durometer hardness test is used for measuring the relative hardness of soft materials. The test method is based on the penetration of a specified indentor forced into the material under specified conditions. Higher Durometer hardness readings are considered positive results.

Durometer hardness readings were taken according to ASTM D2240-97 (ASTM 1998). The Durometer hardness tester (Shore Instrument and MFG Co., Freeport, NY) consists of a pressure foot, an indentor, and an indicating device. Two types of durometers are most commonly used —Type A and Type D. Due to the slightly harder sample being examined, the Type D gauge was used. The test was carried out by first placing a specimen on a hard, flat surface. The pressure foot of the instrument was pressed on to the specimen, making sure that it was parallel to the surface of the specimen. The Durometer hardness was read within 1 sec after the pressure foot was in firm contact with the specimen. Each specimen was subjected to 10 Durometer hardness readings, at designated positions on the sample bases. Values for these readings were then averaged. The Durometer hardness measuring instrument is shown in Figure 2.

Fig.2. Durometer hardness testing.

Tensile Impact Strength Test

The impact properties of the polymeric materials are directly related to the overall toughness of the material. The tensile impact strength test was developed to overcome the deficiencies of flexural impact tests. Tensile-impact energy is the energy required to break a standard tension-

impact specimen in tension by a single swing of a standard calibrated pendulum under as set of standard conditions.

Tensile-impact strength test was measured according to ASTM D1822-93 (ASTM 1993). The tensile impact testing machine consists of a rigid massive base with a suspending frame. The pendulum is specially designed to hold the dumbbell-shaped specimen so that the specimen is not under stress until the moment of impact. Figure 3 is a tensile impact tester (Tinius Olsen Testing Machines Co., Willow Grove, PA).

Fig.3. Tensile-impact strength testing.

The specimens are prepared by rotational molding to the desired shape from a sheet. The type L (long) specimen extension is comparatively high. Type L specimens provide a greater differentiation between materials. The Type L (long) specimens were prepared in Figure 4.

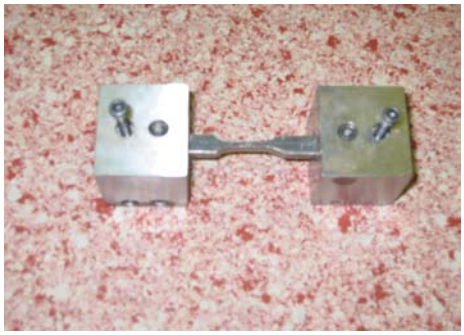

Fig.4. Type L tensile-impact specimens.

Results and Discussion

Tensile Test

Tensile testing was performed with varying methods of chemical pre-treatment of flax fibers in order to develop a sense of how these pre-treatments affected the tensile strength of biocomposites. The tensile strength test was also intended to determine which chemical treatments of flax fiber have a positive effect on the mechanical properties of composites when the amount of fiber was increased (from 10% to 20%). Figure 5-7 show the tensile strength at yield of 10% flax fibers compared to 20% flax fibers-based composites with different types of thermoplastic matrix.

No significant difference in tensile strength at yield was observed between composite specimens having 10% by weight fiber loading, while the tensile strength value of 20% fiber-based composites was improved significantly by the three treatments. This is probably due to the increased fiber-matrix adhesion and amount of flax, which had high tensile strength acting as reinforcing material. When compared across chemical treatments the composites containing peroxide-treated flax fibers had comparable or higher tensile strength than composites containing other chemically treated fibers and untreated fibers. The variation in tensile properties could be explained on the basis of the changes in chemical interactions at the fiber-matrix interface on various treatments. The tensile strength of flax fiber-reinforced composites is determined both by the tensile strength of the fiber and by the presence of weak lateral fiber bonds (Mohanty et al. 2001). The variations in the tensile strength at yield of the composites on different modifications were attributed to the changes in the chemical structure and bondability of the fiber. Also, the tensile properties of natural fiber-reinforced composites could be improved by the use of silane coupling agent. Therefore, the results of this test show that the flax fiber did increase the tensile strength of molded composites.

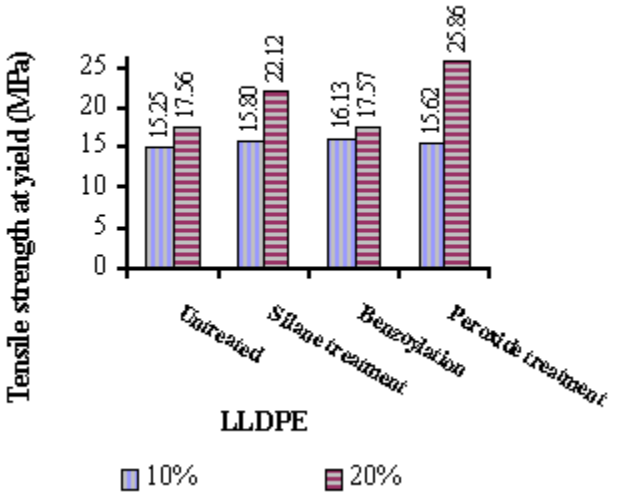

Fig. 5. Tensile strength at yield of 10% flax fibers compared to 20% flax fibers based composites with LLDPE.

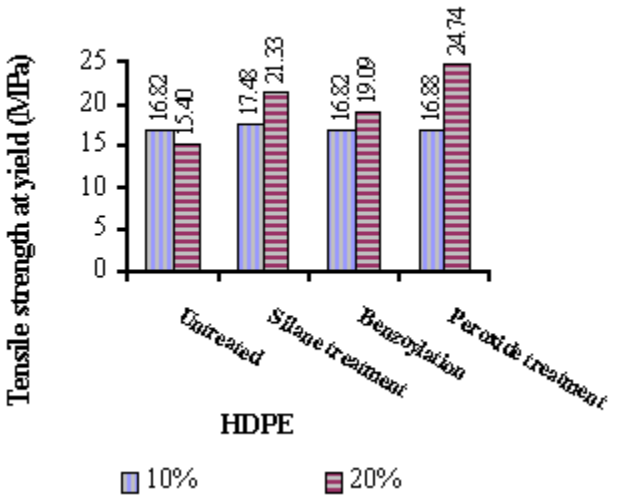

Fig. 6. Tensile strength at yield of 10% flax fibers compared to 20% flax fibers based composites with HDPE.

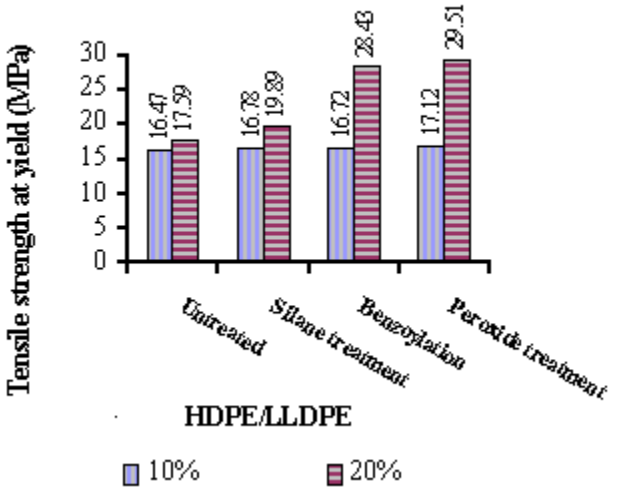

Fig. 7. Tensile strength at yield of 10% flax fibers compared to 20% flax fibers based composites with HDPE/LLDPE.

Durometer Hardness

The data and numerical results from each durometer hardness test are presented in this section. Figure 8-10 show the hardness of 10% flax fibers compared to 20% flax fibers-based composites with different types of thermoplastic matrix.

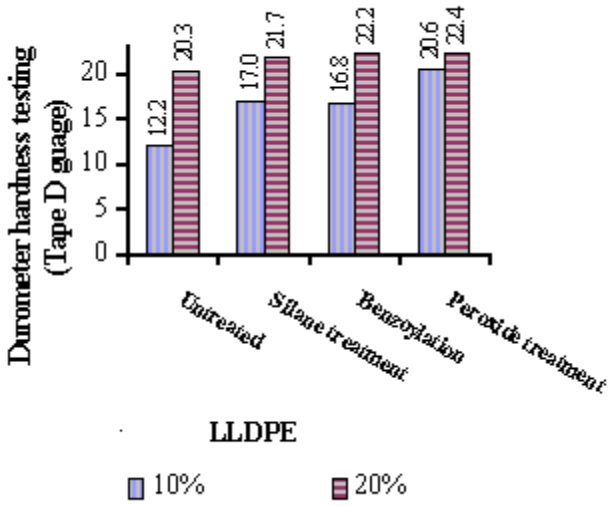

Fig. 8. Hardness of 10% flax fibers compared to 20% flax fibers based composites with LLDPE.

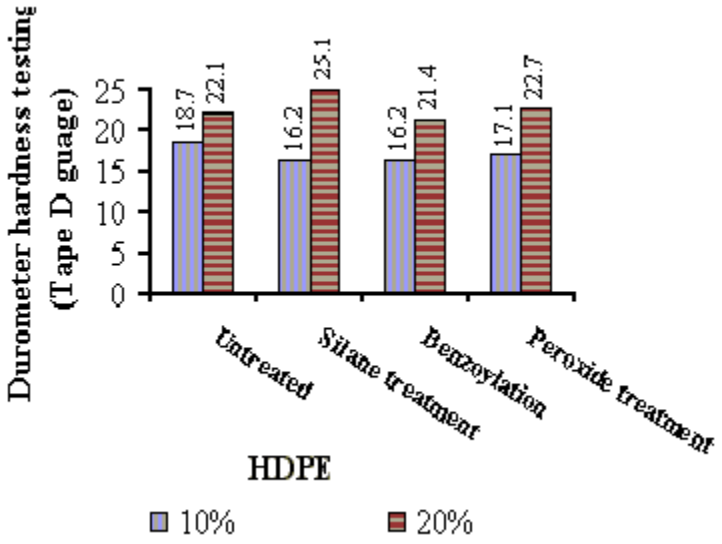

Fig.9. Hardness of 10% flax fibers compared to 20% flax fibers based composites with HDPE.

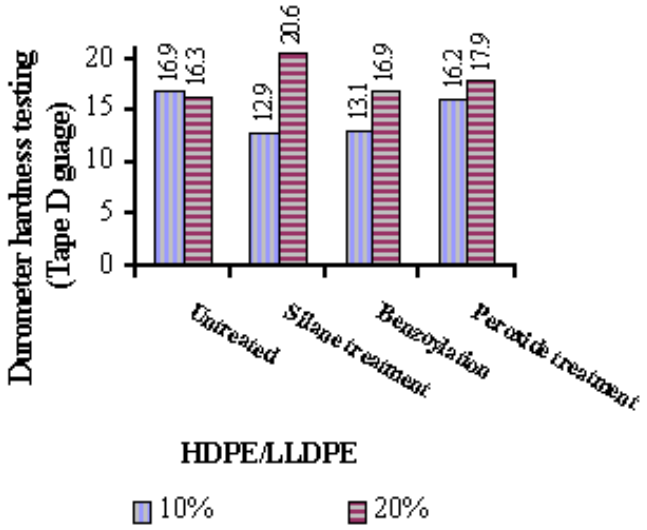

Fig.10. Hardness of 10% flax fibers compared to 20% flax fibers based composites with HDPE/LLDPE.

The hardness of plastics was measured by the Shore (Durometer) test. This method measures the resistance of plastics to indentation and provides an empirical hardness value that does not correlate well to other properties or fundamental characteristics. The hardness value is determined by the penetration of the Durometer indenter foot into the sample. The results obtained from this test are a useful measure of relative resistance to indentation of various grades of polymers.

Ten readings were taken for each specimen, as material properties were expected to vary with location on the sample. For the 10% fiber-based composites, chemically treated flax fibers did not increase the hardness of specimens. However, for the 20% fiber based-composites, all samples performed well. When compared across fiber pre-treatment types, composites containing chemically treated fibers had higher hardness than the composites containing untreated fibers. As the amount of fiber was increased (from 10% to 20%), hardness increased, with the exception of the untreated flax fiber with HDPE, as it stayed the same. Therefore, the increased loading of treated flax fibers did increase the hardness of molded composites.

Tensile Impact Strength Test

The tensile-impact strength of 10% pre-treated flax fibers compared to untreated flax fibers based composites with different types of thermoplastic matrix in Figure 11. The influence of chemical modification on the tensile-impact strength of composites is also represented in Figure 11. As observed, the reinforcement of composites with treated flax fiber enhanced the tensile-impact strength of the resulting composite quite significantly. The tensile-impact strength values of untreated fiber-based composites are comparatively lower than with composites as prepared from chemically pretreated-based samples.

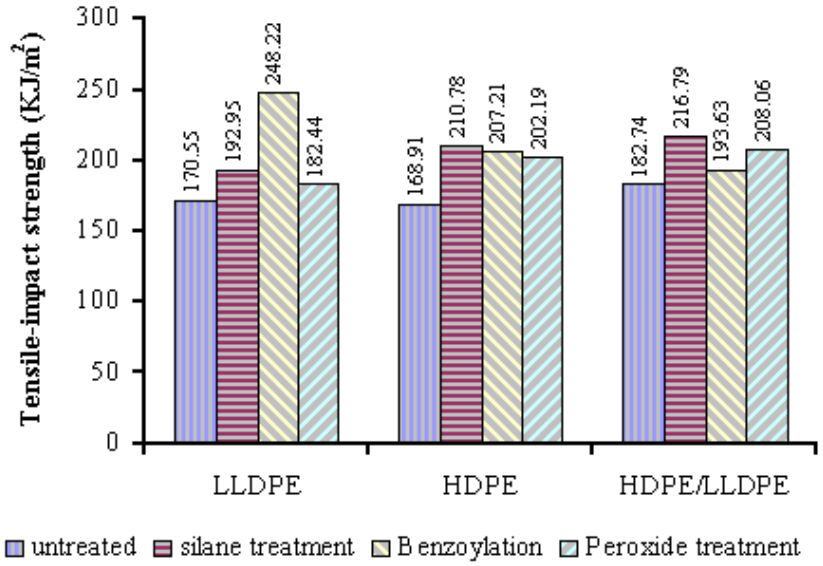

Fig.11. Tensile-impact strength of 10% pre-treated flax fibers compared to untreated flax fibers based composites.

Conclusion

Renewable fibers like flax can be used as reinforcing materials for low cost composites, due to the economic and environmental advantages of such materials. This project focused on determining the ideal chemical pre-treatments and the fiber content of flax fiber-based biocomposite material.

The results showed that fiber content influenced the tensile, hardness and tensile-impact properties. The 20% flax fiber-based composites had higher tensile strength at yield and Durometer hardness than the 10% flax fiber-based composites. Compared to the untreated fiber-based composites, tensile strength, hardness and tensile-impact strength were improved with a suitable fiber surface treatment. Silane, benzoylation, and peroxide treated fiber-based composites offered superior mechanical properties. Mechanical properties of natural fiber-reinforced plastic composites could be improved by the use of silane-coupling agent as well.

In the present study, chemically treated flax fiber is used as filler to plastics, and a reinforcement agent in thermoplastic matrix in rotational molding process. The addition of fibers can result in significant material cost savings, as the fibers are available at a cheaper price than the expensive glass fibers or other inorganic additives. Environment and energy advantages by using natural fibers instead of glass fibers will get more attention in the future.

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